NEW YORK UNIVERSITY
INSTITUTE OF MATHEMATICAL SCIENCES
LIBRARY
~~25 Waverly Place, New York 3, N.Y.~~

NEW YORK UNIVERSITY
INSTITUTE OF MATHEMATICAL SCIENCES
LIBRARY
4 Washington Place, New York 3, N. Y.

New York University
Institute of Mathematical Sciences
~~25 Waverly Place~~, New York 3, N.Y.
4 Washington Place
~~Return postage guaranteed~~

Keller, Joseph B.
Decay of drop by evaporation, and growth by condensation, by Joseph B. Keller, Ignace Kolodner, and Paul Ritger.

c.1

IMM-NYU 183 July 22, 1952

284-2M-1053

IMM - NYU 183 22nd of July, 1952

DECAY OF DROP BY EVAPORATION, AND GROWTH BY CONDENSATION

Joseph B. Keller, Ignace Kolodner, and Paul Ritger

This paper represents results obtained at the Institute for Mathematics and Mechanics under the auspices of the Department of the Army Chemical Corps Contract No. DA- 18 - 064 - CML - 1860 .

I. Introduction

If a liquid (or solid) drop is surrounded by a gas in which the pressure of the drop's vapor is below the equilibrium vapor pressure, the vapor diffuses away from the drop surface and the drop evaporates (or sublimates) . This evaporation, which maintains the vapor pressure near the surface at the equilibrium value, results in the decay of the drop. Conversely, if the vapor pressure in the surrounding gas exceeds the equilibrium value, vapor diffuses toward the drop, condenses on its surface and the drop grows. The same description applies to a drop dissolving or growing in a liquid, if the term "vapor pressure" is replaced by "concentration of solute."

We wish to determine the drop radius and the vapor pressure distribution as functions of time when a single spherical drop evaporates or grows in an infinite motionless gas. In order to do this, we shall formulate the physical problem mathematically in section II. This problem requires that the diffusion equation for the vapor pressure or concentration be solved, subject to conditions on an unknown moving boundary, which must also be found. Previous workers have approximated the problem either by assuming the boundary to be stationary or by employing the static diffusion equation. By treating the exact problem, we find that the first of these approximations is good initially, while the second is good at later stages. Our results are obtained in sections III and compared with these approximations in section IV.

Although the equilibrium vapor pressure or concentration depends upon the radius and the temperature of the drop, we assume it to be constant. Thus our mathematical problem can also be interpreted as one of phase change produced by heat flow, provided we interpret concentration as temperature, diffusion coefficient as heat conductivity, equilibrium concentration as transition temperature, etc. For example, the melting of ice in water, or of any solid in a liquid, is a problem of this type.

In a forthcoming paper we intend to present the extension of the present methods to a collection of drops, and in another, to give the proof of the existence and uniqueness of the solution of the mathematical problem considered herein.

II. Formulation

We consider a single spherical drop of radius $R(t)$ at time t, which has radius a at time 0. If $c(r,t)$ denotes the concentration of vapor at radial distance r from the center of the drop at time t, then we assume that c satisfies the diffusion equation

$$(1) \qquad c_{rr} + \frac{2}{r} c_r = D^{-1} c_t \quad .$$

Here D is the coefficient of diffusion. We further assume that, at the surface of the drop, the concentration is equal to the equilibrium concentration corresponding to the temperature and curvature of the drop, which we denote by $g(t,R)$. We assume $g(t,R)$ is a known function, and will usually assume it to be constant. Thus we have

$$(2) \qquad c(R(t),t) = g(t,R) \quad .$$

The rate of growth or decay of the drop depends upon the rate at which vapor condenses on, or evaporates from it. If ρ denotes the density of the liquid in the drop, then conservation of mass yields

$$(3) \qquad \frac{dR}{dt} = \frac{D}{\rho} c_r(R(t),t) \quad .$$

Finally we assume that the initial concentration is uniform and has the value c_0. Formally we have

$$(4) \qquad c(r,0) = c_0 \ .$$

We list also the initial condition on $R(t)$, which was stated above:

(5) $R(0) = a.$

The problem we consider is that of determining $R(t)$ and $c(r,t)$ for subsequent times, and in particular, of finding the time required for a droplet to disappear completely when evaporation occurs.

To this end we first introduce new dimensionless variables as follows:

$$(6)\quad \begin{cases} \bar{t} = D\,a^{-2}t & \bar{c}(\bar{r},\bar{t}) = (g_0 - c_0)^{-1}[c(r,t) - c_0] \\ \bar{r} = a^{-1}r & h(\bar{t},\bar{R}) = (g_0 - c_0)^{-1}[g(t,R) - c_0] \\ \bar{R}(\bar{t}) = a^{-1}R(t) & \alpha = \rho^{-1}(g_0 - c_0). \end{cases}$$

In these equations the barred quantities are the new dimensionless variables, g_0 is the value of $g(t,R)$ at $t = 0$. (1 - 5) now become, upon introducing (6), the following (all bars have been omitted) :

$$(7)\qquad c_{rr} + \frac{2}{r}c_r = c_t\,, \qquad r > R(t)$$

$$(8)\qquad c(R(t),t) = h(t,R)\,,$$

$$(9)\qquad \frac{dR}{dt} = \alpha\, c_r(R(t),t)\,,$$

$$(10)\qquad c(r,0) = 0\,, \qquad r > 1$$

$$(11)\qquad R(0) = 1\,.$$

In the case of condensation ($\alpha < 0$) $R(t)$ will be an increasing function of t, hence $R(t) > 1 > 0$ for all t, and the region in which $c(r,t)$ is desired will not contain the line $r = 0$. In the case of evaporation, ($\alpha > 0$) it is expected that R will vanish at some finite time t_0. We show that in this case an additional boundary condition,

$$(12)\qquad c_r(0,t) = 0\,, \qquad t > t_0$$

must be satisfied. Indeed, since the line $r = 0$ is included in the region of definition of $c(r,t)$, this function can be extended for r negative. Since our problem has spherical symmetry, $c(r,t)$

must be an even function of r, i.e,

$$c(r,t) = c(-r,t) .$$

Continuity of c and of c_r in the region above the evaporation curve implies then the condition (12) .

III. Solution

Let us first consider the one-dimensional analogue of the present problem. The only difference is that the term $\frac{2}{r} c_r$ is omitted from (1) and (7). If $h(t,R) = 1$, this problem can be solved exactly and has the solution

(13) $$c(r,t) = \left(\int_{z_o}^{\infty} e^{-x^2} dx \right)^{-1} \int_{z}^{\infty} e^{-x^2} dx$$

(14) $$R(t) = 1 + 2z_o \sqrt{t}$$

where the quantity z is defined by

(15) $$z = (r - 1)/2 \sqrt{t} ,$$

and z_o is the unique solution of

(16) $$2z_o e^{z_o^2} \int_{z_o}^{\infty} e^{-x^2} dx = - \alpha .$$

If $\alpha < 0$, z_o is positive and the droplet grows. If $\alpha > 0$, then $z_o < 0$, and the drop evaporates, in which case solution (13-14) applies until the drop is gone. The time required for complete evaporation is obtained from (14) by setting $R = 0$. We find

(17) $$t_o = (2z_o)^{-2} .$$

For $t > t_o$, condition (12) must be also satisfied and this is achieved by adding to $c(r,t)$ equation (13), a compensating part $u(r,t)$ defined as the solution of

(18) $$u_{rr} = u_{tt}$$

(19) $$u(r,t_o) = 0, \quad r \geq 0$$

$$(20) \quad u_r(0,t) = - c_r(0,t) = - \left(\int_{z_o}^{\infty} e^{-x^2} dx \right)^{-1} \frac{1}{2\sqrt{t}} e^{-1/4t} , \quad t>t_o .$$

The compensating part can be easily constructed, but since it is felt only for $t \geq t_o$, it will not affect the determination of the evaporation curve.

For small a, the approximate solution of (16) is

$$(21) \qquad z_o = - \frac{a}{\sqrt{\pi}} .$$

Thus the time required for evaporation, if a is small, is approximately (for the one-dimensional case)

$$(22) \qquad t_o = \frac{\pi}{4a^2} \left(= \frac{\pi \varepsilon^2}{4a^2 D} \right) .$$

The last expression is in dimensional units.

To solve the spherical problem, we employ a solution of (7) and (10) which is similar to (12), but involves an arbitrary function f which is to be determined. This solution is

$$(23) \qquad c(r,t) = \frac{1}{r} \int_{z}^{\infty} f[(z-x)\sqrt{t}]\, e^{-x^2} dx ,$$

z being defined by (15) . (The function f is closely related to the initial value of $c(r,t)$ for $r < 1$; precisely,

$$f\left(\frac{r-1}{2}\right) = \frac{rc(r,0)}{\sqrt{\pi}} , \qquad r < 1 .)$$

In the case of evaporation, the additional boundary condition (12) must be satisfied after the drop disappears. To satisfy this condition we need merely add to (23) a similar expression with $-r$ instead of r after the drop disappears. That this is so is shown in the paper referred to above, which contains the existence and uniqueness proof. This compensating part plays no role, however, in the determination of the evaporation curve.

To determine $R(t)$ and $f(\tau)$, we assume that $R(t)$ may be expanded in a formal power series in $\sqrt{t}$ and $f(\tau)$ in a formal power series in τ , i.e.,

$$R(t) \sim 1 + 2\sum_{n=1}^{\infty} a_n t^{n/2} , \tag{24}$$

$$f(\tau) \sim A_o(1 + \sum_{n=1}^{\infty} A_n t^n) . \tag{25}$$

The expression "formal power series" is used since it will not be established whether any of the series (24) and (25) has a positive radius of convergence. However, it will be demonstrated that our procedure leads to results satisfactory for most practical purposes, regardless of whether the above series converge or do not converge. In any case, the expression (24) for R(t) can not converge up to $t = t_o$, the time at which the drop disappears, and therefore could not be used for determination of t_o. This is evidenced by the fact that $R^2(t)$ behaves like a linear function of t near $t = t_o$ as is shown in the paper referred to in the Introduction, (this is also confirmed by experimental results) and a series of the same type as in (24) cannot exhibit such a behavior.

By means of (25), equation (23) can be rewritten as

$$rc(r,t) = A_o\left(\int_z^{\infty} e^{-x^2}dx + \sum_{n=1}^{\infty} A_n t^{n/2} \int_z^{\infty}(z-x)^n e^{-x^2}dx\right) . \tag{26}$$

The numbers a_n and A_n are now determined by inserting (26) in (8) and (9) and by identifying the coefficients of various powers of $\sqrt{t}$. Thus we find, when $h(t,R) \equiv 1$

$$\left\{\begin{aligned} a_1 &= z_o , \\ a_2 &= -\frac{\alpha + 2(\alpha+1)z_o^2}{\alpha+2(\alpha+1)(1+z_o^2)} , \\ A_o &= \left(\int_{z_o}^{\infty} e^{-x^2}dx\right)^{-1} , \\ A_1 &= 2\frac{\alpha-a_2}{\alpha+1} , \end{aligned}\right. \tag{27}$$

etc., z_o being defined by equation (16). For α small, we have

$$(28)\quad \begin{cases} a_1 = -\dfrac{\alpha}{\sqrt{\pi}} ; & A_0 = \dfrac{2}{\sqrt{\pi}} , \\ a_2 = -\dfrac{\alpha}{2} , & A_1 = 3\alpha , \\ a_3 = -\dfrac{\alpha^2}{3\sqrt{\pi}} , & A_2 = -2\alpha , \\ a_4 = -\dfrac{(10+3\pi)\alpha^3}{12\pi} , & A_3 = \dfrac{4\alpha^2}{3} . \end{cases}$$

As already stated, the series (24) for R(t) can at best yield information about the local behavior of R(t) for t small. To obtain an approximate result over the full range of variation of t, $0 \leq t \leq t_o$, we now define the N'th approximation $c_N(r,t)$ to $c(r,t)$ by

$$(29)\quad rc_N(r,t) = A_o\left(\int_z^\infty e^{-x^2}dx + \sum_{n=1}^{N} A_n t^{n/2} \int_z^\infty (z-x)^n e^{-x^2} dx\right) ,$$

with the A_n previously computed.

The N'th approximation $R_N(t)$ to R(t) is defined by requiring that the mixed condition

$$(30)\quad [rc(r,t)]_r = c(r,t) + rc_r(r,t) = 1 + \frac{1}{\alpha} R \frac{dR}{dt} , \qquad r = R(t) ,$$

derived from (8) and (9), be satisfied exactly by $c = c_N$ and $R = R_N$. The equation determining $R_N(t)$ is thus

$$(31)\quad 1+\frac{1}{2\alpha}\frac{d}{dt}\left(R_N^2(t)\right) = A_o\left(-\frac{1}{2\sqrt{t}} e^{-z^2} + \sum_{n=1}^{N} \frac{n}{2} A_n t^{\frac{n-1}{2}} \int_z^\infty (z-x)^{n-1} e^{-x^2} dx\right)$$

where
$$z = \frac{R_n(t) - 1}{2\sqrt{t}} , \qquad \text{and } R_N(0) = 1 .$$

C_N and R_N so defined satisfy equations (7), (10), and (11), and the sum of (8) and (9) exactly. Furthermore (8) and (9) are satisfied with an accuracy increasing with N for small t, and for every N, $R_N^2(t)$ is linear in t near $t = t_o$.

Equation (31) has been integrated numerically for N = 1,2,3 and $\alpha = 2 \times 10^{-5}$, corresponding to the case of water drop in air at temperature of 73°F , assuming the vapor pressure at infinity

to be zero. The results listed in the table below show an excellent rate of convergence.

Since $z(0) = z_o \sim -\frac{a}{\sqrt{\pi}}$, and $z(t_o) = -\frac{1}{2\sqrt{t_o}}$, it is expected that z is a small number for all t and may be replaced in (31) by zero, at least for N small. The resulting equation for $\overline{R}_N$ which approximates $R_N(t)$ is

$$(32) \quad 1+\frac{1}{2a}\frac{d}{dt}(\overline{R}_N^2) = A_o\left(-\frac{1}{2\sqrt{t}} + \sum_{n=1}^{N}(-1)^n \frac{n}{4}\Gamma\left(\frac{n}{2}\right)A_n t^{\frac{n-1}{2}}\right),$$

and yields

$$(33) \quad \overline{R}_N^2 = 1-2at + 2aA_o\left(-\sqrt{t} + \sum_{n=1}^{N}(-1)^n \frac{n}{2n+2}\Gamma\left(\frac{n}{2}\right)A_n t^{\frac{n+1}{2}}\right).$$

Comparison with results of numerical integration of the more accurate equation (31) shows again a good agreement.

From (33), we easily deduce that in the three-dimensional case

$$(34) \qquad t_o = \frac{1}{2a}\left(1 - \frac{8}{3\sqrt{2\pi}}\sqrt{a} + O(a)\right),$$

and that to a good approximation,

$$(35) \qquad R^2(t) = 1 - 2at - \frac{4}{\sqrt{\pi}}a\sqrt{t}, \quad \text{for } 0 \leq t \leq t_o .$$

The table below lists the values of $R^2(t)$ computed from the series (24), $R_1^2(t)$, $R_2^2(t)$, and $\overline{R}_1^2(t)$, $\overline{R}_2^2(t)$ to four significant figures, for $a = 2 \times 10^{-5}$. To this approximation, $R_3(t) = R_2(t)$, and $\overline{R}_3(t) = \overline{R}_2(t)$.

t	R^2(eq.24)	R_1^2	R_2^2	$\bar{R}_1^2$	$\bar{R}_2^2$
0	1	1	1	1	1
$.5 \times 10^3$	.9791	.9790	.9790	.9790	.9790
1	.9590	.9586	.9586	.9586	.9586
2	.9197	.9180	.9181	.9180	.9181
4	.8436	.8370	.8370	.8371	.8373
6	.7712	.7563	.7562	.7565	.7568
8	.7021	.6757	.6755	.6760	.6764
10	.6362	.5952	.5949	.5955	.5961
12	.5735	.5148	.5143	.5151	.5159
14	.5142	.4344	.4337	.4347	.4357
16	.4581	.3540	.3531	.3543	.3555
18	.4053	.2736	.2725	.2739	.2754
20	.3557	.1932	.1919	.1936	.1953
22	.3094	.1128	.1113	.1133	.1153
24×10^3	.2662	.0325	.0307	.0330	.0352
t_0		2.481×10^4	2.476×10^4	2.482×10^4	2.488×10^4

Formula (34) yields for t_0 the value 2.488×10^4 .

IV Comparison With Previous Approximate Solutions

An approximation, expected to be valid initially, can be obtained by assuming that $R(t) \equiv 1$ and solving (7), (8), (10) for $c(r,t)$. From this solution $c_r(1,t)$ can be computed and used in (9) to determine an improved $R(t)$. This yields the beginning of a solution in powers of α.

We easily find that

$$(36)\quad c(r,t) = \frac{2}{\sqrt{\pi}\,r}\int_z^\infty e^{-x^2}\, h\left(t-\left(\frac{r-1}{2x}\right)^2, 1\right)dx \;,$$

$$(37)\quad R(t) = 1 - \frac{2\alpha}{\sqrt{\pi}}\sqrt{t} - \frac{2\alpha}{\sqrt{\pi}}\int_0^t h_t\,(t,1)dt - \alpha\int_0^t h(t,1)dt \;.$$

If $h(t,1) = 1$, this becomes

$$(38)\quad R(t) = 1 - \frac{2\alpha}{\sqrt{\pi}}\sqrt{t} - \alpha t \;.$$

Comparison with (24) and (28) shows that we have here the beginning of the asymptotic expansion for $R(t)$ near $t = 0$, provided α is small.

Another approximation, the so-called quasi-static approximation is expected to be valid in the later stages of the process. It is obtained by first neglecting the term c_t in (7) and the initial condition (10). Then, from (7), (8) and from the assumption that c tends to zero as r becomes infinite (which rplaces (10)), we find

$$(39)\quad c(r,t) = \frac{h(t,R)R(t)}{r} \;.$$

Using (9), we find

$$(40)\quad R^2(t) = R^2(\tau) - 2\alpha\int_\tau^t h(t,R(t))dt, \quad \tau \text{ arbitrary} \;.$$

This is an integral equation for $R(t)$ if h depends upon R, but is an explicit solution if h is independent of R. With $R(t)$ so determined, $c_t(r,t)$ may be computed and used again in (7) to obtain an improved $c(r,t)$. When $h \equiv 1$, (40) yields

$$(41)\quad R^2(t) = R^2(\tau) - 2a(t - \tau)$$
$$= 1 - 2at + b \quad ,$$

where $b = R^2(\tau) + 2a\tau - 1$. If $\tau = 0$, then $b = 0$ by condition (11), although this value of b cannot be used since the quasi-static solution does not apply initially. Actually, comparison with (35) shows that a good agreement in the later stages is found if b is chosen as $-2\sqrt{\frac{2a}{\pi}}$. Physically this means that the drop first evaporates quite rapidly until the static concentration distribution is established and then behaves quasi-statically, starting with a smaller radius.

From the fact that the first approximation above agrees with experimental data on the initial growth (decay) of particles, and also agrees with our solution, we conclude that our solution also agrees with the data initially. Similarly, since at later times the quasi-static approximation agrees with evaporation data and with our solution, we conclude that our solution agrees with these data. Thus we expect that our solution will agree with experiment over the entire time range in either evaporation or growth.

Date Due

[illegible]

[illegible]

7/[illegible]

3/20/61

8/15/61

11/20/62

APR 5 [illegible]

5-14 64

5/16/66 ILL

Bel Tel Labs Inc

6 June Brookhaven

JUL 2[illegible]

JAN 1[illegible] 1970 RENEWED

PRINTED IN U. S. A.